ELECTRON EMISSION FROM MICROWAVE-PLASMA CHEMICALLY VAPOR DEPOSITED CARBON NANOTUBES

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ABSTRACT

A microwave plasma CVD reactor was used for the deposition of carbon nanotubes on substrates. Hydrocarbon or oxyhydrocarbon mixtures were used as the carbon source. Hot electrons in the microwave plasma at temperatures exceeding 10,000C provided a means of dissociating the vapor or gas feedstock, heating the substrate, and allowing gas species to react in the gas phase as well as on the surface of the substrate leading to the deposition of desired carbon coatings. A high vacuum chamber was used to characterize the electron emission properties of these carbon nanotube coatings using a one-millimeter diameter tungsten rod with a hemispherical tip as the anode while the carbon nanotube coatings served as the cathode. The current-voltage characteristics of the carbon nanotube coatings were measured and used for calculating the electric field at which electron emission turned on as well as calculating the field enhancement factor of the carbon nanotubes. Field emission of electrons from carbon nanotubes starting from an electric field lower than 1 volt per micrometer has been achieved.

INTRODUCTION

Micro-engineering in the nano-meter scale using carbon atoms as the building block has resulted in amazingly excellent characteristics of cabon-based structures that finds broad applications ranging from microelectronics to cutting tools. One of these amazing carbon materials is CVD diamond that has been intensively studied in the past fifteen years or so. More recently, the science and practical applications of carbon nanotubes became popular because of its equally great commercial and technological potentials.

Carbon, when properly arranged in a 3-dimensional order, forms the hardest materials on earth, diamond. In addition to being an attractive gemstone, diamond is the champion in almost every aspect of materials properties. Its thermal conductivity is five times better than copper at room temperature making it an excellent material as the heat spreader for high power density integrated circuits. Its bandgap energy is higher than SiC and most of compound semiconductors making it desirable for fabricating high power density electronic devices or sensors and actuators for operation in high-temperature and radiation hostile environments. Its super hardness and chemical inertness make it an economic material for cutting tools or simply used as protective coatings.

By building carbon structures in the nano-meter scale, it is possible to make carbon tubes that are as small as a few nanometers in diameters and are formed by layers of graphite-like carbon structures. When these carbon nano-tubes are coated on a smooth or porous substrate with a conductive surface layer, they emit electrons without needing to be heated to such a high

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Microwave plasma was applied to convert hydrocarbon and oxyhydrocarbon mixtures into favorable mixtures of species for the nucleation and growth of carbon nanotubes on various substrates that were pre-seeded with catalysts. Carbon Nanotubes with excellent electron emission characteristics have been deposited at a substrate temperature ranging from 600 to 1,000C. Field emission of electrons from carbon nanotubes starting from an electric field below 1 volt per micrometer has been achieved.

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temperature as a hot tungsten filament cathode in a vacuum tube is usually done. It, therefore, becomes a very promising material for the application as a cold cathode for flat panel displays or other electron devices.

A number of methods for chemical vapor deposition of diamond based on different gas mixtures and energy sources for dissociating the gas mixtures have been reported [1]. These techniques include the use of high-temperature electrons in various kinds of plasmas, high-temperature surfaces of hot filaments, and high-temperature gases in combustion flames to dissociate molecular hydrogen, oxygen, halogen, hydrocarbon, and many other carbon containing gases. The substrate is usually maintained at a temperature much lower than that of electrons in plasma, the hot filaments, or the combustion flame, resulting in a super equilibrium of atomic hydrogen near the diamond-growing surface.

Most of diamond CVD processes involve in the use of one or more compressed gases. The most typical example is the use of 1% methane gas diluted by 99% hydrogen. These gases usually must be precisely controlled using electronic mass flow controllers to ensure an accurate composition in the gas feed. Diamond CVD using a microwave plasma CVD reactor and a liquid feedstock without any compressed gas was also reported [2].

Chemical vapor deposition of carbon films in the form of carbon nanotubes is not much different from that for the CVD of diamond. The key experimental parameter for the coating of carbon nanotubes instead of diamond or diamond-like carbon films is the presence of suitable catalysts for carbon nanotubes to grow in the gas phase or on the substrate. In this paper, a microwave plasma reactor that was designed and used for diamond deposition was used for depositing carbon nanotubes on metal substrates for electron emission studies. Oxyhydrocarbon vapor or hydrocarbon gas mixtures were used as the feedstock.

EXPERIMENTS

Shown in Figure 1 is the schematic diagram for the microwave plasma CVD reactor that was used for this study. Hydrocarbon or oxyhydrocarbon mixtures were fed into a vacuum chamber that was evacuated by a mechanical pump. The chamber gas pressure was controlled by a throttle vale and a manometer pressure gauge. An rod antenna was used to couple microwave power from a rectangular waveguide into a cylindrical metal cavity through a quartz window that separate the atmosphere from the vacuum chamber. The microwave power formed a plasma ball on the top of the substrate. Electrons in the plasma have very high temperatures exceeding 10,000° C. The plasma heated the substrate to a preset temperature as well as heated the gas mixtures for proper dissociation and reaction in the gas phase leading to carbon deposition on the substrate surface. Copper, nickel, and Cobalt were used as the catalysts for the carbon coatings to grow into carbon nanotubes instead of forming diamond-like carbon coatings.

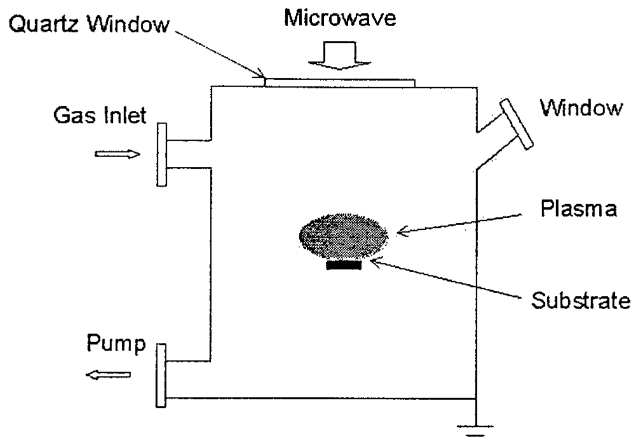

Figure 1. Schematic diagram of the microwave plasma CVD apparatus.

The carbon nanotube coated substrates were then loaded into a high vacuum chamber shown in Figure 2 that was pumped down by a turbomolecular pump and an ion pump to a vacuum of about 1×10^{-7} Torr . The carbon nanotube coated substrate served as the cathode while a tungsten rod of one-millimeter diameter with the tip grounded into a hemispherical shape was used as the anode. The distance between the anode and the cathode was adjusted using a linear vacuum feedthrough to move the tungsten rod closer or farther from the carbon nanotube coated substrate. A desktop computer controlled the output of a high-voltage power supply for applying a voltage between the anode and the cathode. The electric field is calculated by dividing the applied voltage by the gap spacing between the anode and the cathode. The electron emission current was measured by a digital ammeter and recorded by the computer for further plotting and calculation.

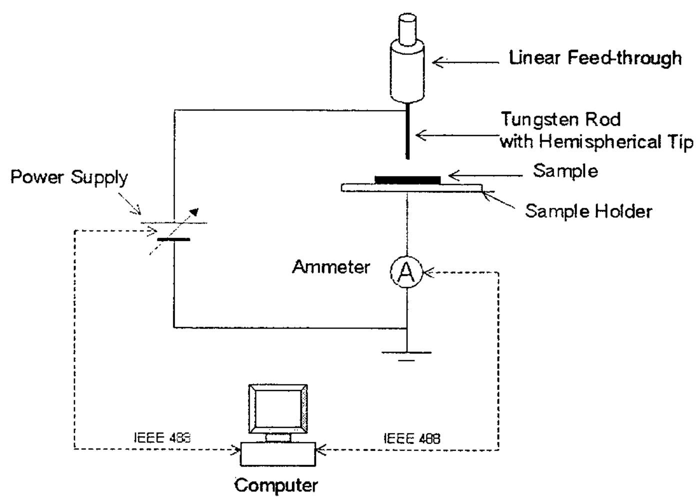

Figure 2. Experimental setup for electron emission measurement.

RESULTS

Shown in Figure 3 is the SEM photograph for carbon nanotubes coated on a nickel plate using microwave plasma CVD technique. The electron emission

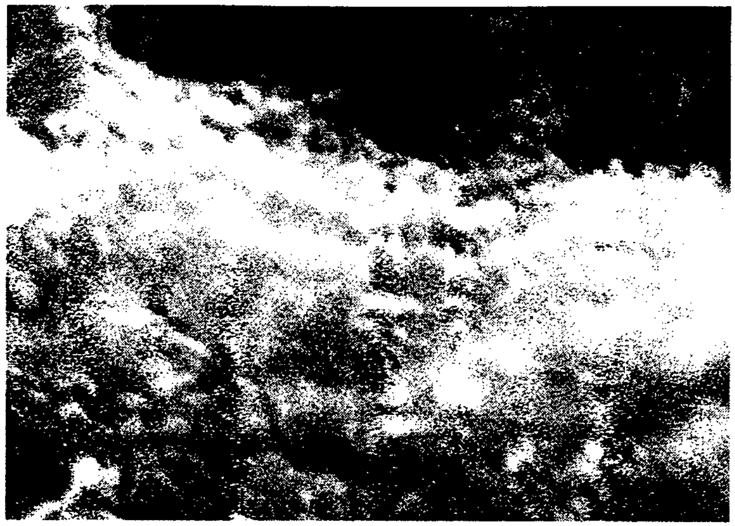

Figure 3. SEM photograph for carbon nanotubes coated on a nickel plate.

characteristics for this carbon nanotube coated nickel substrate are shown in Figure 4 and 5. The carbon nanotube coating was fabricated in 90 minutes at a temperature around 900° C in an oxyhydrocarbon plasma powered by 900 watts of microwave at 2.45GHz at a gas pressure of 36 Torr . The gap spacing between the tungsten rod and the nanotube coating for electron emission measurement was 495 micrometers. Figure 3 shows that field emission of electrons started at an electric field equal to about 0.9 volt per micrometer. Electron emission current rose exponentially at electric field higher than the turn-on field of 0.9 volts per micrometer. The slope decreased at the electric field about 1.5 volts per micrometer and started to become saturated.

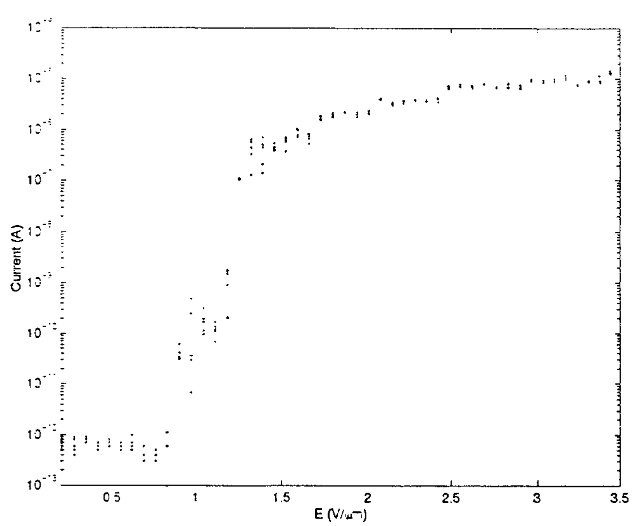

Figure 4. Field emission electron current vs. electric field.

The Fowler-Nordheim plot of the data is shown in Figure 5. A well-defined region of negative slope appears prior to the region of emission current saturation. The field enhancement factor was calculated from the negative slope using 5 eV emission barrier for graphite to be 2840.

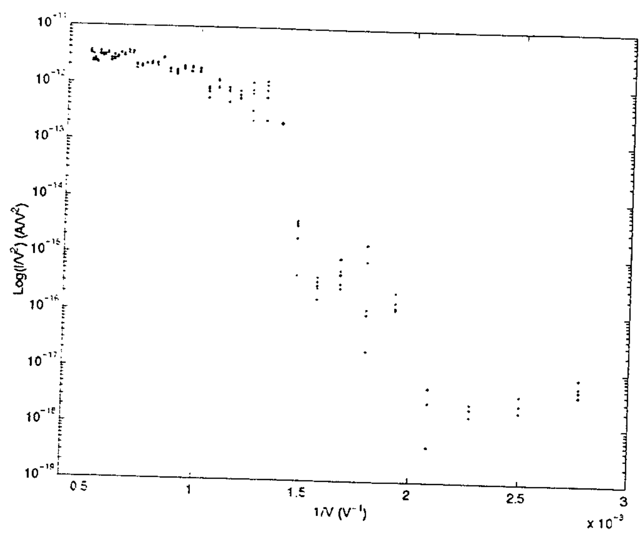

Figure 5. Fowler-Nordheim plot for field emission electron current.

DISCUSSION

The fabrication processes for CVD diamond and carbon nanotube coatings are similar. Microwave plasma CVD technique provides a means of producing very high temperature electrons for dissociating species that are difficult to be dissociated by a hot filament. From Figure 3 and 4, it is clear that the emission mechanism is of the Fowler-Nordheim type with electron field emission commencing at a low electric field because of the 2840 times of field enhancement factor [3-4]. The small diameter and very high aspect ratio of the carbon nanotube make it possible for the local electric field at the tip of the carbon nanotube to be more than two thousand times higher than that calculated by dividing the applied voltage by the distance between the anode and the carbon nanotube coating. With optimization of the coating conditions and the proper choice and applications of catalysts, high electron emission current exceeding 1 A per square centimeter at an electric field lower than 1 volt per micrometer is achievable.

CONCLUSIONS

Carbon nanotube with threshold electron emission electric field lower than 1 volt per micrometer has been coated using a microwave plasma CVD reactor similar to the one that was used for depositing CVD diamond. This is the lowest reported threshold electric field for electron emission from a cold carbon nanotube. Field emission results from carbon nanotube coatings showed clearly the Fowler-Nordheim behavior.

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REFERENCES

1. Y. Tzeng, A. Feldman, Y. Yoshikawa, and M. Murakawa, eds., Applications of Diamond, Elsevier Publishers, Netherlands (1991).
2. Y. Tzeng, Proceedings of Applied Diamond Conference/ Frontier Carbon Technology Joint Conference 1999, Eds. M. Yoshikawa, Y. Koga, Y. Tzeng, C.-P. Klages, and K. Miyoshi, MYU, K.K., Tokyo, Japan (1999), pp.20-24.
3. W. Zhu, C. Bower, O. Zhou, G. Kochanski and S. Jin, Appl. Phys. Lett. **75**, 873 (1999)
4. G. A. J. Amarutunga, M. Baxendale, N. Rupesinghe, M. Chhowalla, and I. Alexandrou, Proceeding of Applied Diamond Conference/ Frontier Carbon Technology Joint Conference 1999, eds. M. Yoshikawa, Y. Koga, Y. Tzeng, C.-P. Klages, and K. Miyoshi, MY, K.K., Tokyo, Japan (1999), pp. 335-339.